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CAMERON STATION, ALEXANDRIA, VIRGINIA

ASD-TDR-63-804

# INVESTIGATION OF FIRE EXTINGUISHING AGENTS FOR SUPERSONIC TRANSPORT

TECHNICAL DOCUMENTARY REPORT ASD-TDR-63-804

September 1963

SUPERSONIC TRANSPORT RESEARCH PROGRAM
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Research and Technology Division
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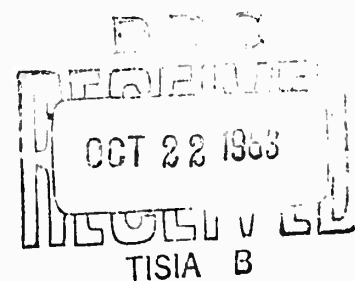
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FOREWORD

ABSTRACT

Properties of ten compounds which have passed screening for possible use in the in-flight fire extinguishing system of the Supersonic Transport are tabulated. Reported are boiling points, freezing points, densities, viscosity-temperature relationships, vapor pressure-temperature curves, critical temperatures and pressures, heats of vaporization, specific heats, pressures at 500°F and thermal stabilities under testing conditions. Also reported are the inhibitory effects of each compound on heptane-air flammabilities, estimated costs and compatibilities with various metallic and non-metallic materials. Potential toxicities are discussed.

Limited physical properties of an additional twenty-four materials which did not pass this preliminary screening are tabulated. Recommendations are given for more extensive work on acceptable compounds to further define their usefulness under Supersonic Transport flight conditions.

This technical documentary report has been reviewed and is approved.

for Marc P. Dunnam
Chief, Technical Support Division
AF Aero Propulsion Laboratory

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I. SUMMARY

Presently used extinguishants will not be satisfactory for use under conditions expected to prevail upon storage in the Supersonic Transport. Thermal stabilities of these materials are too low or extinguishant pressures are too high for use in a low pressure system at temperatures generated during flight.

Listed in this report are ten compounds which have passed screening under specifications set up for the Supersonic Transport in-flight fire extinguishing agent. None represents an ideal extinguishant from a consideration of all properties desirable in this use. This is because the molecular features, which may lead to a desirable property, may at the same time, cause enhancement of an undesirable property. As an example, the specifications of low agent vapor pressure at $500°F$ and of low agent viscosity at $-65°F$ are not mutually compatible. The increase in molecular weight within a halocarbon series giving low vapor pressures will increase low temperature viscosities. Compounds listed then are compromises of desirable features.

Reported for these compounds are boiling points, freezing points, densities, viscosity-temperature curves, vapor pressure-temperature curves, critical temperatures, critical pressures, heats of vaporization, specific heats of the liquids, pressures at $500°F$ and thermal stability limits under various conditions utilized. Also reported for each acceptable compound are its inhibitory effects on flammability of heptane-air mixtures. This is a pre-fire test indication of its extinguishing capability. The flammability inhibition data is used to roughly predict extinguishant effect relative to chlorobromomethane on weight and volume bases. Estimated costs of the ten agents are also included. Limited work on compatibility of these agents with materials of construction is reported as well as an abstract of a literature survey of halogenated fluorocarbons not obtained in this work but having structures making them sufficiently thermally stable for screening if additional compounds are desired. Samples of acceptable compounds have been submitted for preliminary toxicological testing.

A listing of an additional twenty-four materials screened, but not found acceptable, is part of this report with data which may not be available in the literature. These data may be useful to workers in other fields, so are appended here.

Recommendations are given for more extensive screening of the reported ten compounds. This program would further define useful thermal stability data, attempt to improve viscosities and stabilities, determine materials compatibility and moisture sensitivity under flight conditions, and investigate the possibility of utilizing these extinguishants in conjunction with a presently used extinguishant for better low temperature coverage.

II.   INTRODUCTION

The purpose of this work is to delineate materials suitable for use in the in-flight extinguishing system of the Supersonic Transport. The agent is specified to have the following properties.

1.   Suitable for use in combating hydrocarbon and electrical fires. The weight effectiveness of the agent shall be preferably comparable to presently utilized halogenated hydrocarbons.

2.   No more toxic than methyl bromide.

3.   Suitable for use at -65°F to temperatures approaching 500°F.

4.   Shall be stable in storage under recurring anticipated Supersonic Transport flight conditions as well as ground climatic conditions for up to three years.

5.   Capable of production at reasonable cost and with existing production facilities.

6.   No more corrosive than bromochloromethane.

7.   Shall be a nonconductor of electricity.

8.   Shall have suitable pressure-temperature characteristics making the agent utilizable in a low rate discharge system. This assumes a total system pressure of 400 psia (nitrogen plus agent) at 70°F. System pressure for the purpose of this investigation at 500°F should not exceed a maximum of 1660 psia. This specification is selected so that present agent containers might be utilized. It is subject to change if system analysis shows a high rate discharge system and higher pressures are more desirable. Low temperature volatility and viscosity of the agent should approach those of chlorobromomethane for effective discharge at -65°F.

Presently used extinguishing agents do not satisfy the listed specifications. For example, chlorobromomethane is applicable for extended use only in the range -65°F to 250°F, dibromodifluoromethane in the range -65°F to 350°F, bromochlorodifluoromethane in the range -65°F to 400°F and bromotrifluoromethane is usable above 500°F. However, vapor pressures of the latter two materials at 500°F are so high (Table I, Section III-A) as to preclude their use in a low pressure system.

During the course of this work, the TriAgency Panel authorized addition to the list of agents to be reported, those with thermal stabilities between 350°F and 500°F. Such compounds may possibly be con-

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sidered acceptable for use if agent storage conditions are later found to be below those believed now to prevail or if insulation of storage containers is allowed as a means of lowering flight temperatures to which agent will be exposed. Other compounds which do not satisfy vapor pressure requirements but which have acceptable thermal stabilities have been added by NESCO.

Since mechanisms of flame propagation in fuels to be used in the proposed transport will be the same as for fuels now in use, the problem of developing new agents devolved to one of retaining the various chemical groups which are known to inhibit combustion while at the same time, changing over-all molecular structures to increase thermal stability and molecular weight. Higher molecular weights are necessary to reduce the vapor pressures.

It has been found that halocarbons containing bromine or iodine are superior hydrocarbon flame inhibitors. The hydrogen halides or halide atoms produced in their decomposition terminate flame chain reactions by capturing appropriate free radicals in the flame front, such as hydrogen atoms and hydroxyl radicals which are among the chain propagating radicals in a hydrocarbon-air flame. Bromine and iodine in halocarbons are more effective for this purpose than chlorine or fluorine (1). However, fluorine within the halocarbon has been found necessary to lend thermal stability to the fire suppressant and to lower its toxicity. It appeared, then, that the logical extinguishants to be used at $500^{\circ}F$ should be fluorocarbons containing bromine or iodine. Since organo iodides are less thermally stable than bromides, the bromides were considered the most likely candidates with the more thermally stable but less effective chlorocarbons as less desirable candidates. Other inhibitors for hydrocarbon flames such as iron carbonyl, lead tetraethyl, phosphorus trichloride and titanium tetrachloride, though more effective than organo halides (2), are toxic and could not be considered for use.

A literature survey of brominated and chlorinated fluorocarbons revealed little information is available on low temperature properties or on thermal stabilities of such compounds. Boiling points, densities and indices of refraction were generally the only physical properties listed. The complete literature survey was part of the first quarterly report on this contract. An abstract, listing compounds with structures, which on the basis of this work are now believed necessary for thermal stability, is included. These compounds were not available during this work. Low temperature properties cannot be predicted with any certainty and these listed compounds (Section III-C-9) may not be suitable because of deficiencies in this regard.

Commercial, government and university laboratories active in the field of fluoroorganics were solicited for samples of compounds possibly satisfying specifications set forth above. In addition, catalogs

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of chemical suppliers were consulted and compounds purchased for testing. NESCO synthesized additional materials believed possibly useful for this application.

The program of screening involved evaluation of the low temperature properties of all materials. Where a material was solid or obviously highly viscous at $-65^{\circ}F$, it was eliminated from further testing. If the material had suitable low temperature properties, its thermal stability was investigated. If the material was thermally stable at a minimum of $350^{\circ}F$ (see Section III-C-1) a vapor pressure-temperature curve was obtained and density, boiling point and specific heat (liquid) were measured (Section III-C-2, 3, 4). Its critical temperature and heat of vaporization were calculated and critical pressure and agent pressure at $500^{\circ}F$ obtained from the vapor pressure curve.

The effect of the material on the flammability of n-heptane-air mixtures was measured in a modification of the apparatus evolved by the Purdue Research Foundation (3, 4). This method, described in Section III-C-5, gives flammability curves with peaks at the minimum volumetric concentration of inhibitor at which no mixture of heptane and air will propagate a flame. A ranking of agent effectiveness is obtained which may be roughly correlated with actual extinguishing effectiveness. These correlation studies were made by the Engineer Research and Development Laboratories (5). Although there is controversy over the validity of flammability peak data in the evaluation of extinguishants on actual fires (6), the technique is useful for a pre-fire test screening.

Compounds which are reported were tested for compatibility with several metallic and nonmetallic materials of construction wet and dry under ambient conditions. Time did not permit testing under the more significant high temperature storage conditions.

Approximate price estimates for six of the reported compounds were obtained from potential suppliers. Four other reported compounds were synthesized by NESCO. These are previously unknown compounds, are not commercially available, and no manufacturer contacted would estimate their cost. The price given for these materials, then, is a NESCO estimate based on cost of intermediates.

The list of materials was submitted to ASD Aeromedical Division which reports there is no record of toxicological properties being measured for any compound on the list. Samples of seven of the ten materials have been submitted to ASD for evaluation.

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III. RESULTS

A. Compounds Satisfying Specifications

Compounds 1, 2 and 4 of the ten compounds in Table I listed as satisfying specifications, do not actually satisfy the requirement of a 940 psia maximum pressure at $500^{o}F$, however, since thermal stabilities of these compounds were in a satisfactory range, they are included against the possibility that system analysis may allow a change in the agent pressure requirement. All data in the Table were obtained by methods described in following Sections III-C-1 to 7 and general discussions of these results are contained under each of these sections.

Vapor pressures for these materials are plotted in Fig. 1, viscosities in Fig. 2 and inhibitory effects on heptane-air flammability in Figs. 6-9. Data on compatibility of agents with various materials are tabulated in Tables V and VI. Comments on costs, availability and toxicity are contained in Sections III-C-7 and 8.

Some literature (6) data for the extinguishants CF_3Br, $CBrClF_2$ and CF_2Br_2 are included for comparison purposes. It is noted that if storage tanks could be insulated to maintain storage temperatures in the $250-350^{o}F$ region, that bromochlorodifluoromethane and dibromodifluoromethane would be below their critical temperatures and their thermal stability limits. They may then be of possible use in a higher pressure system than contemplated under the specifications listed in Section II. It is to be noted, however, that dibromodifluoromethane has been found to be a central nervous system depressant (6) in laboratory animal tests.

Data on inhibitory effect, called extinguishing capability, are merely for pre-fire test screening purposes. Significance of these results was discussed in Section II. For comparison purposes, these data are related to combustion buret data obtained for chlorobromomethane on a weight basis by dividing by the inhibitory effectiveness of CB (Column headed "Wt. Req. Rel. to 1 lb CB). The next column gives an estimated cost for this weight. The data on inhibition effectiveness are related on a volume basis to CB by dividing the weight relative to CB by each agent's density (Column headed "Vol. Equiv., 1 lb CB = 0.519).

The International Union of Chemistry rules for nomenclature (7) have been used for naming compounds 1 - 10 and these names are listed in Table I.

In Table II, the extinguishants are ranked by property and a numerical total ranking value obtained (last column) by adding individual ranking numbers. There is little advantage seen for any of

	Compound	MW	BP °F	FP °F	Density 77°F	Critical Temp.°F	Critical Pressure (psia)	Thermal Stability Limit, °F	$\Delta H_{vap.}$ K-Cal/Mol
1	$H(CF_2)_2CH_2Cl$	150.5	133	-112	1.199	480	970	550	6.90
2	$CFCl_2CHCl_2$	186	102	-112	1.622	433	840	375	7.24
3	$H(CF_2)_2CH_2Br$	195	163	-112	1.631	527	1080	475	7.79
4	$CF_3CBrClH$	197.5	126	-112	1.870	469	928	400	7.03
5	$CF_2BrCFBrH$	242	169	-112	2.274	540	1260	350	7.60
6	$H(CF_2)_4CH_2Cl$	250.5	221	-112	1.325	618	815	550	8.38
7	$CCl_3CF_2CFCl_2$	270.5	309	-121	1.779	757	290	500	8.94
8	$CF_2BrCFBrCl$	276.5	194	-99	1.428	577	1085	375	8.36
9	$H(CF_2)_4CH_2Br$	295	245	-112	1.883	656	970	550	9.27
10	$CF_2BrCFClCF_2CFClH$	314	279	-112	1.950	710	540	525	10.71

* Figures in parentheses are extinguishant vapor pressures at 70°F (psia)

** Assumes system pressure of 400 psia at 70°F

CF_3Br		149	-72	-282	1.57	154	574	500	4.20
$CBrClF_2$		165	25	-257	1.83	309	565	400	5.29
CF_2Br_2		210	73	-223	2.28	390	593	350	5.93

Nomenclature of Above Compounds

1) 1-Chloro-2,2,3,3-tetrafluoropropane
2) 1,1,2,2-Tetrachloro-1-fluoroethane
3) 1-Bromo-2,2,3,3-tetrafluoropropane
4) 1-Bromo-1-chloro-2,2,2-trifluoroethane
5) 1,2-Dibromo-1,1,2-trifluoroethane
6) 1-Chloro-2,2,3,3,4,4,5,5-octafluoropentane
7) 1,1,1,3,3-Pentachloro-trifluoropropane
8) 1,2-Dibromo-1-chlorotrifluoroethane
9) 1-Bromo-2,2,3,3,4,4,5,5-octafluoropentane
10) 1-Bromo-2,4-dichloro-1,1,2,3,3,4-hexafluorobutane

TABLE I

PROPERTIES OF CANDIDATE EXTINGUISHANTS

Critical Pressure (psia)	Thermal Stability Limit, °F	$\Delta H_{vap.}$ K-Cal/Mole	Specific Heat - Liquid Cal/Deg-Gm	Exting. P. 500°F (psia)*	System P. 500°F (psia)**	Exting. Capability. Wt/100 l Heptane-Air CB = 43.9 g	Wt. Required to Obtain Exting. Effect of 1 lb CB	Est. C... for This... Rel. 1 l...
970	550	6.90	0.61	1080 (4.8)	1790	82.6	1.88	
840	375	7.24	0.55	1140 (5.0)	1850	36.6	0.83	1.
080	475	7.79	0.54	680 (2.4)	1400	45.3	1.03	
928	400	7.03	0.42	1025 (4.5)	1735	30.7	0.70	Approx
260	350	7.60	0.38	720 (1.8)	1440	36.8	0.84	Approx
815	550	8.38	0.58	200 (0)	925	104.2	2.37	
290	500	8.94	0.60	90 (0)	815	78.5	1.79	Approx
085	375	8.36	0.38	500 (0)	1225	55.5	1.26	Approx 3
970	550	9.27	0.49	300 (0)	1025	99.0	2.25	3
540	525	10.71	0.46	250 (0)	975	51.8	1.18	Approx 2
574	500	4.20		2725	3450			
565	400	5.29		2100	2760			
593	350	5.93		1160	1860			

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ting. P. 00°F sia)*	System P. 500°F (psia)**	Exting. Capability. Wt/100 l Heptane - Air CB = 43.9 g	Wt.Required to Obtain Exting. Effect of 1 lb CB	Est. Cost for This Wt. Rel. 1 lb CB	Vol. Equiv. 1 lb CB = 0.519	Est. Cost Per lb
80 (4.8)	1790	82.6	1.88	25	1.57	15
40 (5.0)	1850	36.6	0.83	1.60	0.51	2
0 (2.4)	1400	45.3	1.03	15	0.63	15
25 (4.5)	1735	30.7	0.70	Approx 3	0.37	4
0 (1.8)	1440	36.8	0.84	Approx 7	0.66	8
0 (0)	925	104.2	2.37	30	1.79	15
(0)	815	78.5	1.79	Approx 11	1.01	6.50
0 (0)	1225	55.5	1.26	Approx 3	0.88	2.25
0 (0)	1025	99.0	2.25	30	1.20	15
0 (0)	975	51.8	1.18	Approx 22	0.61	20
25	3450					
00	2760					
50	1860					

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FIGURE 1

VAPOR PRESSURE CURVES OF AGENTS

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FIGURE 2

VISCOSITIES OF CANDIDATE EXTINGUISHANTS

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TABLE II

RANKING OF CANDIDATE EXTINGUISHANTS BY PROPERTIES

Compound	Increasing BP	FP	Increasing Viscosity (-65°F)	Decreasing Density	Decreasing Crit.Temp.	Decreasing Specific Heat	Decreasing Thermal Stability	Increasing Exting. Pressure 500°F	Increasing System Pressure 500°F	Exting. Effect Wt.Basis	Exting. Effect Vol.Basis	Total (Unweighted)
1 $H(CF_2)_2CH_2Cl$	3		2	10	8	1	1	8	8	8	9	63
2 $HCCl_2CFCl_2$	1	All	1	7	10	4	7	9	10	2	2	60
3 $H(CF_2)_2CH_2Br$	4	Approx.	8	6	7	5	5	6	6	4	4	58
4 $CF_3CBrClH$	2		3	4	9	8	6	8	9	1	1	57
5 $CF_2BrCFBrH$	5	Same	4	1	6	10	8	7	7	3	5	57
6 $H(CF_2)_4CH_2Cl$	7		7	9	4	3	1	2	2	10	10	63
7 $CCl_3CF_2CFCl_2$	10		9	5	1	2	4	1	1	7	7	57
8 $CF_2BrCFBrCl$	6		6	8	5	9	7	5	5	6	6	65
9 $H(CF_2)_4CH_2Br$	8		5	3	3	6	2	4	4	9	8	56
10 $CF_2BrCFClCF_2CFClH$	9		10	2	2	7	3	3	3	5	3	56

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the agents in this ranking. A greater spread in total ranking number, allowing elimination of some of the compounds from further testing, would be obtained by weighting individual ranking numbers for more important properties such as viscosity, critical temperature, thermal stability, system pressure and extinguishing capability.

B. Compounds Not Suitable for Further Testing

The sequence of screening tests was outlined in Section II and details of procedures with discussion are contained in Sections III-C-1 to 7. It will be noted that most compounds in Table III were unsuitable because of sub-specification low temperature properties or thermal stabilities. If either of these specifications is liberalized, it is possible that several of these compounds may then be considered for use.

Since most of the data in Table III is not available in the literature, it is included in this report for workers in other fields.

Haloesters of halogenated acids had been tested because of their ready availability compared to halocarbons. These compounds did not show sufficient thermal stability to be of use. Fluorophosphate esters were of interest because of the flame inhibitory properties of phosphorus compounds. They displayed excellent thermal stability when the β carbon was fluorine blocked but the low temperature viscosity characteristics were poor.
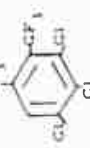
Completely fluorinated compounds, as might be expected, were thermally stable, but were poor inhibitors compared to those compounds containing bromine and/or chlorine.

The thermal stability of the one benzene derivative tested was surprisingly poor and the mechanism of decomposition is not evident. Comments on the relation of structure and thermal stability are contained in Section III-C-1.

Several compounds were not available in sufficient quantity to screen completely. Structures indicated they should be thermally stable but should not be more than average flame inhibitors. For these reasons, $CF_3CF_2CF_2CCl_3$ and $CF_2ClCFClCF_3$ were not included in Table I.

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TABLE III

PROPERTIES OF MATERIALS TESTED BUT NOT FOUND SUITABLE

Compound	MW	B.P.(°F)	F.P.(°F)	Density/°C	Viscosity (C.S.)/°C	Thermal Stability Limit(°F)	Inhibiting Effect: Heptane-Air g/100 liters	ΔHVap K-cal/M	P550°F psi	n/°C	Reason For Rejection	Comments
$BrCl_2CO_2CH_2CF_3$	221	248-252	>-90	1.68/24		<350				1.3905/22	Poor ther. stab.	
$BrCH_2CO_2CH_2CF_2CF_2H$	253	351			24.4/-28; 2.1/25; 0.67/25			9.99	327	1.3976/22	Poor ther. stab.	
$H(CF_2)_6CH_2Br$	395	192/67 mm; 352/760	>-80	1.874/22		>500	83.6	10.69	263	1.3349/22	Poor low temp. properties	
$BrCF_2CFClCHClCH_2Cl$	294.5	351	-94	1.815/27	2.25/25; 0.79/100	<350		11.49	164	1.458/27	Poor ther. stab.	
$CH_3CHBrCO_2CH_2CF_3$	235	248-253	>-112	1.655/22		<350				1.3917/22	Poor ther. stab.	
$CF_3CO_2CH_2CH_2CH_2CH_2Br$	235	298-305	-62			<350				1.4266/22	Poor ther. stab. and poor low temp. properties	
$CF_3CF_2CF_2CCl_3$	287.5	198	-102	1.678/24		>500	64.5			1.3457/25	Poor inhibitor	Possibly promising but quant. not avail. for further testing
$CF_3CF_2CFClCH_2Cl$	235	185	-126	1.613/24		<350				1.3396/25	Poor ther. stab.	
$CF_3(CF_2)_5CHF_2$	370	203	-80	1.723/25				2.96		1.2700/25	Poor inhibitor	
$(CF_3(CF_2)_3)_3N$	671	347-356	-87	1.872/20			219			1.2910/25	Poor inhibitor	
$CF_2BrCFClCH_2CH_2Br$	304.5	331		2.068/24		<350				1.4580/25	Poor ther. stab.	
[aromatic (chlorinated) structure]	317.5	370	-80			<350		5.39		1.5027/25	Poor ther. stab.	
$CF_2ClCFClCF_3$	221	95	-136	1.5896/20						1.3029/20	Too high vap. pressure at 500°F	Possibly promising but quant. not avail. for further testing
KEL F-1	av. 500	range	>-72	1.84/25			145	10.7		1.400/25	Poor inhibitor	
$(CF_3CH_2O)_3P$	344	140-158/10mm	visc -40	1.608/25		>550	96.7			1.3225/18	Poor low temp. properties	
$CFClBrCFBrCFClCFCl_2$	426	392 decomp				<350					Poor ther. stab.	
$H(CF_2)_8CH_2Cl$	450.5	mp.102-126									Solid	
CF_2BrCF_2Br	260	115				<350					Poor ther. stab.	
$CF_2BrCFClH$	197.5	124	>-112	1.8638/25		<350				1.3685/25	Poor ther. stab.	
$CFCl_2CFCl\text{-}CF=CFCl_2$	301.5	275	-70							1.4275/23	Poor low temp. properties	
$CCl_3CF_2CFClBr$	315	349	-76							1.4642/23	Poor low temp. properties	Possibly usable if low temp. spec. liberalized
Vinyl Bromide Telomer	range	<385				<350					Poor ther. stab.	
$CHBrCl_2$	164	192-194		1.992/26	0.55/25	<350	40.3			1.4963/20	Poor ther. stab.	
$(HCF_2CF_2CH_2O)_3P$	424	401	visc -40	1.675/27	37.4/25; 3.7/99	>550		7.46		1.3450/21	Poor low temp. properties	

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C. Experimental Conditions Utilized

1. Thermal Stability Measurements

a. Experimental Method, Discussion and Recommendations

A two cc sample of the material was placed in a stainless steel bomb with a needle valve for evacuation and a needle valve leading to a pressure gauge. The bomb was cooled in liquid nitrogen or dry ice and evacuated on the mass spectrometer high vacuum system till the instrument pressure reading was zero (less than $3\,\mu$). The bomb was closed, warmed, frozen again and re-evacuated. It was placed in an oven up to the needle valve block and heated to $350^{o}F$ for 18 hours, then removed, cooled and the pressure measured by opening the needle v alve to the gauge. No acceptable material developed more than 2 atmospheres pressure during heating. The bomb was then cooled in liquid nitrogen and noncondensable gases analyzed mass spectrometrically. Noncondensables were then pumped out, the residue warmed and then analyzed mass spectrometrically. The bomb was then opened and the volume of the residue measured and the material inspected. A gas chromatographic spectrum of the residue was compared to that of the agent before heating. The bomb was washed out with acetone and the washings inspected for evidence of decomposition.

An arbitrary limit of thermal stability was chosen at recovery of at least 1.8 cc of clear material out of the 2.0 cc charge. An additional limit was that there be less than $10^{o}/o$ decomposition evidenced in gas chromatographic analysis of the residue, i.e., although $90^{o}/o$ of the sample might be recovered, if the recovered material on analysis showed $10^{o}/o$ decomposition products, it was judged thermally unstable at the temperature utilized. Fresh 2.0 cc samples of agents were heated to 375°, 400°, $425^{o}F$, etc., until failure to pass the test was observed. Materials which discolored on heating were listed as suitable. However, this discoloration may be indicative of polymer formation and even small amounts of solid polymer, not detectable in this work on small scale, may clog valves in an extinguishing system.

Because of the small quantities of materials available for this screening program, it was not possible to perform experiments which could be extrapolated to quantities which will be present in actual agent storage cylinders. Long heating times or accelerated testing to approximate three year agent use under flight conditions were not possible because such long term experiments, even if accelerated, would have preempted ovens and pressure cylinders needed for continuation of the screening program.

The significance of the stability testing method utilized here as more than a screening guide is difficult to assess since agent thermal stability has not been a serious problem previously. More useful data would be obtained from other experimental procedures such as the following:

(1)   Differential Thermal Analysis (8, 9, 10) - where temperatures at which gross thermal degradations occur are indicated by major exotherms or endotherms in thermograms that show energy profiles of the decomposition reactions. This method will not give any information on rates of decomposition below that at which gross decomposition occurs and must be coupled with long term heating at the lower temperatures to determine agent life below decomposition temperatures.

(2)   Time-Temperature-Solids Deposition - this method has been used for investigating the thermal stability of aviation turbine fuels (11) and involves pumping the material through a heater, then through a filter where solid degradation particles are trapped. The extent of coking is noted as a pressure drop across the filter and in combination with the deposit condition of the heater, is used as an assessment of the thermal stability. This method must be coupled with long term heating at temperatures below those at which gross decomposition occurs or a method of accelerated storage testing to determine storage life under flight conditions.

(3)   Time-Temperature-Agent Viscosity Change - this would be the method used to determine storage life when the decomposition temperature has been determined by either method 1 or 2. It is doubtful that decomposition would not be accompanied by viscosity changes but to check this, the method should be accompanied by an agent analysis procedure such as gas chromatography.

It is possible that the presence of anti-oxidants as additives may enhance the thermal stability of some of the agents which show stabilities below $500^{\circ}F$ in the screening procedures reported here. Those agents that produce hydrogen halides by intermolecular reaction mechanisms may decompose at a faster rate through catalytic action of the hydrogen halide. Catalytic decomposition might also occur in the presence of metallic halides from reaction of the storage container and hydrogen halides. This catalytic effect was noted in this work when several materials with low vapor pressures were heated in glass containers and evidenced less decomposition than when heated in stainless steel. It is recommended, then, that anti-oxidants such

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* E. I. DuPont Freon Bulletin B-2 lists temperatures for first traces of decomposition in quartz for CCl_3F as $840^{\circ}F$; for CCl_2FCClF_2, $570^{\circ}F$; for CCl_2F_2 as $1000^{\circ}F$. All temperatures are 300 to $750^{\circ}F$ higher than those listed for these compounds in the presence of oil, steel and copper.

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as organo tin compounds be tested to determine whether agent thermal stability can be increased through use of additives.

The effect of moisture on agent thermal stability or corrosivity was not investigated in this work and it is recommended that this experimental work be performed with agents selected for further testing.

In the event that a mixture of a low temperature agent suitable for high rate discharge (such as bromotrifluoromethane) and a high temperature agent from this screening program is selected for testing, it will be necessary to subject such a mixture to thermal stability evaluation. It is not anticipated that there should be synergistic effects on decomposition with such materials.

b.   Structure and Stability

From the data of this work, the following generalizations are obtained:

(1)   Halocarbons containing hydrogen and either bromine or chlorine on adjacent carbon atoms will eliminate hydrogen bromide or chloride on heating at 350 to 400°F.

(2)   Compounds containing bromine atoms on adjacent carbon atoms will thermally eliminate bromine at $350-400^{\circ}$F. The compound CF_2BrCF_2Br would be expected to be more stable than $CF_2BrCFBrH$ (which was marginal for inclusion in Table I) but inexplicably was not. The compound $CF_2BrCFBrCl$ was slightly more stable than $CF_2BrCFBrH$.

(3)   Compounds containing hydrogen and either bromine or chlorine on the same carbon will be thermally stable if adjacent carbon atoms are fluorinated. This appears to be due to the impossibility for intramolecular elimination of hydrogen halides. Compounds 1, 3, 6, 9 and 10 of Table I are examples of such structures and are stable at 475°F to greater than 550°F. Inexplicably, the compound $H(CF_2)_2CH_2Br$ (No. 3) is less stable (475°F) than $H(CF_2)_4CH_2Br$ (No. 9) (550°F) though intramolecular elimination of hydrogen bromide leading to ring formation, is spacially more feasible in the latter than in the former.

(4)   Perfluorochloro compounds are stable at least to 500°F under conditions utilized. E. I. DuPont Company, in Freon Technical Bulletin B-2, gives as maximum temperatures for continuous exposure in the presence of oil, steel and copper the following: For CCl_3F and CCl_2FCClF_2, 225°F; for CCl_2F_2 and $CClF_2CClF_2$, 250°F; for $CHClF_2$, $275-300^{\circ}$F and for $CClF_3$, above 300°F.

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For decomposition rates in per cent per year at 400°F in steel, this bulletin lists for the compounds CCl_3F, CCl_2FCClF_2, CCl_2F_2 and $CClF_2CClF_2$, 2%, 6%, less than 1% and 1%. These latter data would appear to corroborate statement 4 above.

2. Vapor Pressure, Heat of Vaporization, Critical Temperature, Critical Pressure, System Pressure

The compound was sealed into a bulb attached to a Stock valve U tube which could be filled from a mercury reservoir. The mercury closed the valve at high pressures to prevent vapor loss. The U tube was connected to a mercury manometer. The bulb and the U tube containing mercury were totally immersed in a silicone oil bath which was heated. For high vapor pressures, air was admitted to the external manometer to approximately balance the vapor pressure of the liquid. The air pressure read on the manometer was added to the pressure difference in the Stock valve U tube. The pressure readings were made with a cathetometer.

The heat of vaporization was obtained from the vapor pressure curve using the Clausius-Clapeyron equation. The critical temperature was estimated from the boiling point using the relationship $T_{bp}\,^{\circ}K/T_{crit}\,^{\circ}K = 0.63$. Experimentally obtained critical temperatures for $CBrClF_2$, CBr_2F_2, $CBrF_3$, and CF_2BrCF_2Br all satisfied this relationship according to our calculations and it was assumed to be applicable to the related halocarbons of this work. The critical pressure was taken from the extrapolated vapor pressure curve at the calculated critical temperature.

Pressures at 500°F for $H(CF_2)_2CH_2Cl$, $HCCl_2CFCl_2$ and $CF_3CHBrCl$ (Compounds 1, 2 and 4) were calculated from the Dieterici equation of state:

$$(p\, e^{\dfrac{a}{\widetilde{V}RT}})\ \ (\widetilde{V} - b)\ =\ RT$$

where

$$p_{crit} = \frac{a}{29.56\,b^2}\ ;\ \ T_{crit} = \frac{a}{4\,b\,R}\ ;\ \ \widetilde{V}_{crit} = 2\,b$$

Values for critical pressure and critical temperature were taken from vapor pressure curves to solve for a and b. These three compounds have critical temperatures below 500°F.

Pressures at 500°F for all other compounds were taken from the extrapolated vapor pressure curves (Fig. 1). System

pressures at 500°F were obtained by subtracting agent pressure at 70°F from 400 psia and calculating what the resultant 70°F nitrogen pressurization would be at 500°F using the ideal gas laws. The sum of agent pressure at 500°F and nitrogen pressure at 500°F gave the system pressure. Effect of system size and amount of agent (fill ratio) has been neglected in all calculations.

3. Density, Freezing Point and Viscosity

Densities were measured at 70°F in a calibrated pycnometer. No studies of density-temperature relationships were made during this screening program. For system analysis, such measurements will be necessary to determine volume changes during flight conditions.

Freezing points were only roughly determined for most compounds since fluidity at dry ice temperatures $(-112^{\circ}$F$)$ was considered as sufficient to allow for further testing. Low temperature viscosities were considered more important than freezing point. Freezing points of compounds not fluid at -112°F were determined by immersing a sample in a freon-12 bath cooled to -100°F, then allowing the bath to warm to the melting point of the agent. Materials were eliminated from further consideration if melting points were above -70°F.

Viscosities were measured in Ostwald viscometers calibrated against standard glycerol-water mixtures. Viscosities obtained were in centistokes and were converted to centipoises by multiplying by agent density for comparison with data for known extinguishants. The values for known extinguishants given in Fig. 2 are from Ref. 12. The data listed in this cited publication are noted to have an estimated accuracy of ± 30 %. Since the low temperature viscosities reported here and presumably in the cited work, use densities at 70°F for calculations rather than actual higher densities at the low temperatures, the viscosities given are probably low.

Low temperature viscosities, shown in Fig. 2, were obtained by immersing the viscometer, protected with Drierite drying tubes in a large clear glass Dewar containing freon-12 cooled to the desired temperature of measurement with liquid nitrogen. Temperatures were measured with a pentane thermometer checked for accuracy with dry ice $(-112^{\circ}$F$)$ and a chloroform slush $(-81.4^{\circ}$F$)$.

As would be expected, the compounds, because of their higher molecular weights, have higher viscosities than the halogenated methanes. Since discharge rate and atomization will be functions of viscosity, it is recommended that additives to improve viscosities be investigated. Surface active agents of the non-ionic type might be effective in lowering surface tensions and improving atomization characteristics of these agents.

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4. Specific Heat

A Dewar cylinder, 2-1/2 inches by 9 inches, was equipped with a cork, a thermometer calibrated in tenths of a degree centigrade, and a glass stirrer. The heat capacity of the system was then determined by the following method. An aluminum rod heated in boiling water was added to a weighed amount of water in the system. The time, in seconds, and the temperature were observed as many times as possible during the period of increasing temperature. Thus the time at which the maximum temperature occurred was observed. The rate of cooling was determined and a correction, equal to the cooling rate multiplied by the time to the maximum temperature, was added to the maximum temperature. Since the heat capacities of aluminum and water are known, and the heat lost by the aluminum must equal the heat gain by the system, the heat capacity of the calorimeter was calculated.

The calorimeter was then emptied and dried and the procedure was repeated for each of the samples. Since the heat capacity of the calorimeter was known, it was possible to calculate the heat capacities of the various samples. In the latter cases, the aluminum rod was heated in an oven for over one hour. The long heating period was necessary to obtain consistent results. The heat capacities reported are considered accurate to the second decimal place.

Because of the low boiling points of most of the agents, no attempt was made to determine temperature dependence of specific heat. All measurements were made on liquids heated to approximately $30-35^\circ$C. ($86-95^\circ$F).

5. Extinguishant Capability - Effect of Materials on Heptane-Air Flammability

The effect of inhibitors on flammability of heptane-air mixtures has been roughly correlated with the fire extinguishing action of the inhibitor (3, 4, 5). Since the inhibitors tested in this program were less volatile than those utilized in the work reported by the Purdue Research Foundation, it was necessary to modify the apparatus which was previously used (3) in determining inhibitory effect.

In Fig. 3 is shown a diagram of the equipment and photographs are shown in Figs. 4 and 5.

The entire metal manifold system and the pressure measuring device were heated to 398°F by means of heating tapes. The combustion tube was custom fabricated by Corning Glass Company and is a conductive glass tube of 50 mm diameter. The large end was graded sealed to a removable brass flange, th bottom of which contained a tungsten wire sealed through glass for ignition (Detail, Fig. 5).
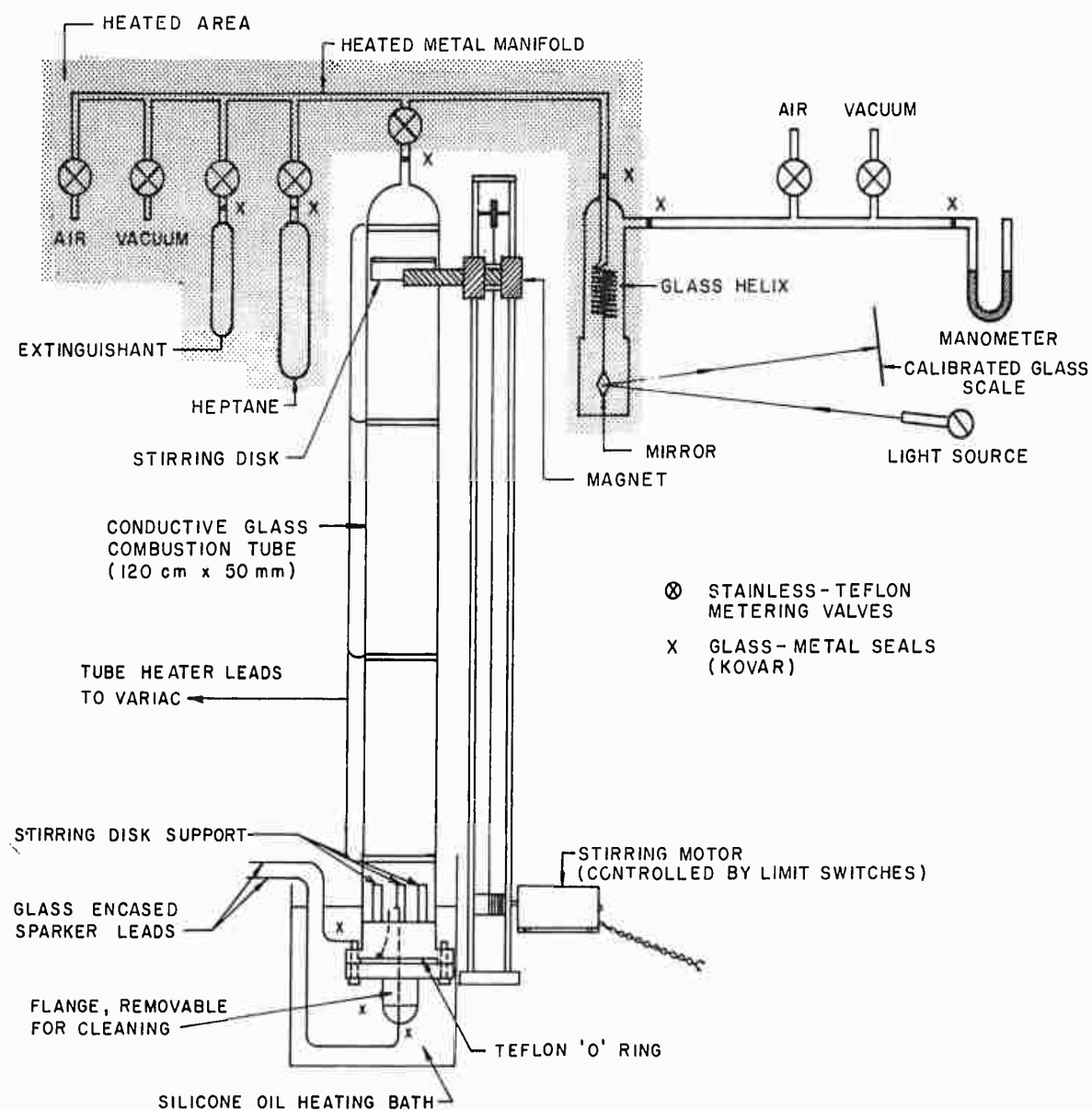
22

FIGURE 3

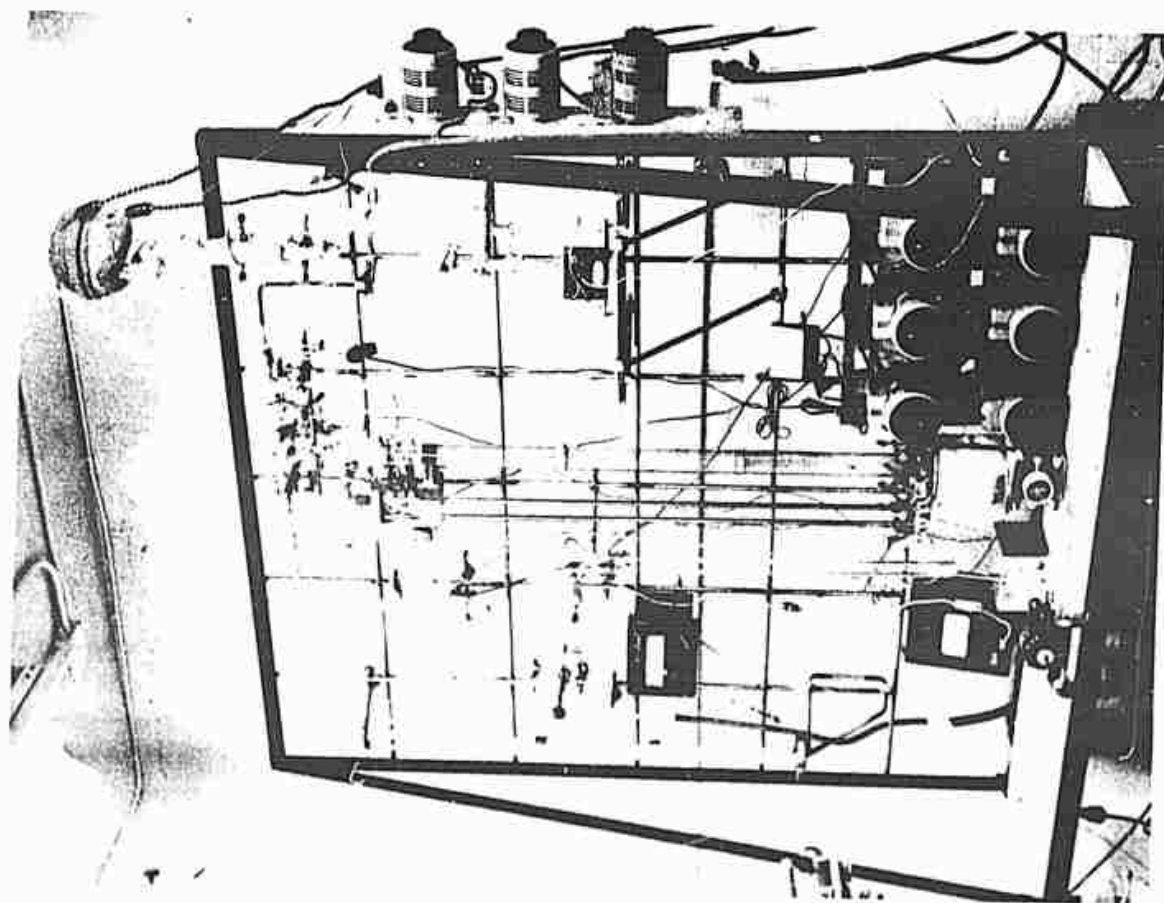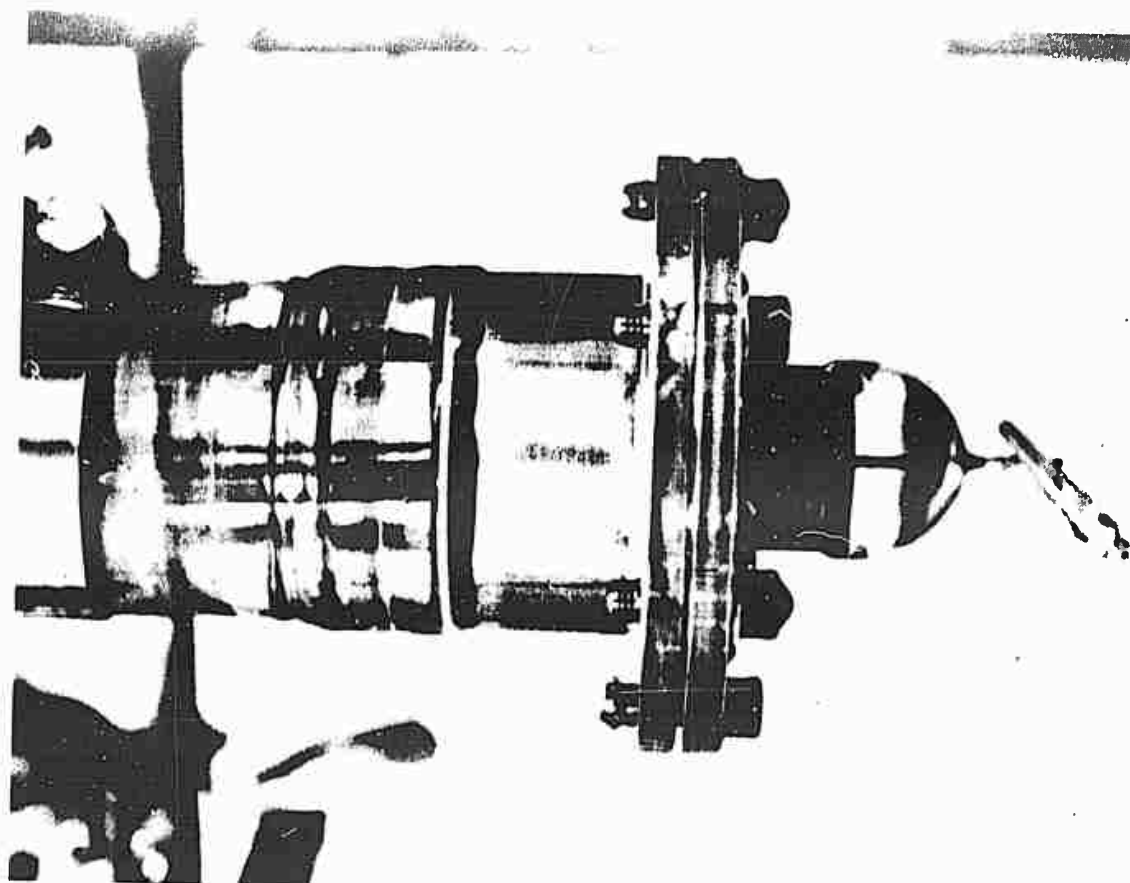COMBUSTION TUBE FOR FLAMMABILITY LIMIT STUDIES (DIAGRAM)

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FIGURE 5   FLANGE DETAIL

FIGURE 4   COMBUSTION TUBE

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The bottom of the tube beyond the resistance coating was heated in a silicone oil bath to $398^\circ F$. Mixing of inhibitor, heptane and air was accomplished by means of a hollow aluminum cylinder with perforated bottom. The cylinder was wrapped with iron wire and externally driven by a magnet. The top of the tube was connected by a kovar-glass seal to stainless steel Swagelok fittings and needle valves.

The procedure was to admit the inhibitor to the heated combustion tube to a predetermined pressure. The pressure measuring device is a Kern-Springham manometer (13) containing a glass spiral with attached mirror. Rotation of the spiral deflects the mirror and the deflection is measured on the scale. The spiral deflection was calibrated to read pressures directly up to approximately 50 mm against an external mercury manometer which was read with a cathetometer.

The combustion tube valve was closed and inhibitor in the manifold pumped out. Then heptane was admitted to the tube to a predetermined pressure and the tube closed while the manifold was evacuated. The tube pressure was brought to 300 mm (inhibitor, heptane air) with heated air by utilizing the manometer as a null device: three hundred mm of air, measured on an external manometer, was admitted to the external side of the spiral and the scale subsequently brought back to zero by admitting air to the combustion tube and internal side of the spiral. The air was preheated in a large bulb by means of Glass Col mantles and heating tapes. The inhibitor-heptane-air mixture was mixed for twenty minutes, the mixing disk brought to the top of the tube, and then the mixture was sparked. If ignition, as evidenced by flame propagation to the top of the tube, did not occur, mixing was continued another five minutes and the mixture was sparked again.

It was generally necessary to remove the bottom flange and clean the tube after the series of tests with each inhibitor since there was considerable black solids deposition during the combustion.

First experiments utilized short mixing times and a mixing disk with many perforations. The ignition characteristics changed considerably when the disk was replaced with one containing five one-quarter inch diameter holes and the mixing time was increased to twenty minutes. As an example, the rich limit for heptane-air was first found to be 7.3 % heptane but later when rechecked in the modified apparatus, it was reproducible at 8.75 % heptane. It is possible, but not likely, that tube wall conditioning also contributed to this change.

To relate inhibitory effect of agents reported here to those of already known extinguishants and to determine effect of combustion tube temperature on peak percentage, a number of agents tested by the Purdue Research Foundation (3) were tested in this work. The

comparison of data is shown below.

COMPARISON OF INHIBITOR PEAK PERCENTAGE DATA

Compound	Purdue University: $80^{\circ}F$	This Work: $398^{\circ}F$
1. CF_3Br	40.57	43.17
2. CF_2Br_2	39.37	75.00
3. CF_2BrCF_2Br	56.87	63.73
4. $CF_2BrCFBrCl$	133.5	55.46

Data are in g. extinguishant required to render 100 liters of inhibitor-heptane-air mixture nonflammable. The wide difference with Compound 2 is due to an impure sample being used in our work (see text). The reason for wide difference with Compound 4 is possible due to an impurity in the Purdue sample.

There appears to be a temperature effect on inhibitor effectiveness but in heptane-air this appears to be less than that noted by Purdue workers for butane-air. The increase in peak inhibitor concentration from $80^{\circ}F$ to $398^{\circ}F$ for heptane-CF_3Br is only about 8 % according to our measurements. The increase for butane-CF_3Br peak percentage was 55 % measured by the Purdue Research Foundation and 34 % as measured in this work. With the differences in the systems utilized in this work and in the Purdue work, the agreement is considered good. The above comparison shows considerable differences in these measurements and those of the Purdue Research Foundation for dibromodifluoromethane and for 1, 2-dibromo-1-chloro-trifluoroethane. The sample of the former utilized in this work was later analyzed and found to contain tetrafluoromethane, and apparently fluoroform and hexafluoroethane. These inert diluents have little inhibitory effect and explain the raised peak percentage observed in this work. The inhibitory effect found in this work for 1, 2-dibromo-1-chlorotrifluoroethane was judged more reasonable than that found in the cited work (3). The compound, because of the presence of a chlorine atom, should be more effective than 1, 2-dibromotetrafluoroethane (as found here) yet the cited work (3) ranks it as considerably poorer.

Plots of flammability as a function of inhibitor-heptane-air percentages are given in Figs. 6-9 and data are summarized in Table IV. Areas under curves represent flammable mixture regions. The agent weight required to render 100 liters of all heptane-air mixtures nonflammable is obtained by converting peak volume percentage to weight: $\text{wgt(g)} = \text{peak percentage inhibitor} \times 100 \times \dfrac{\text{agent mole.wgt.}}{22.4}$.
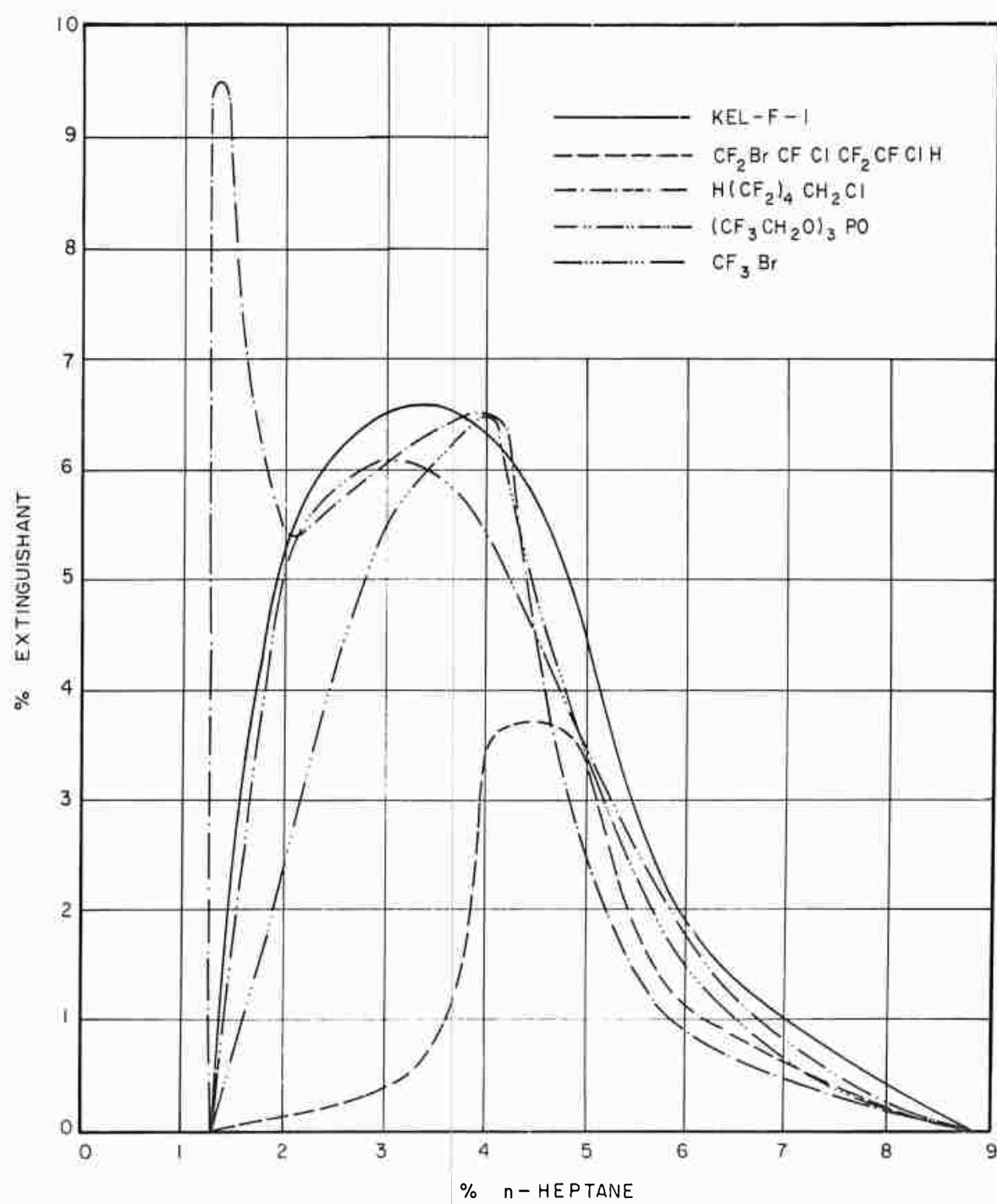
FIGURE 6

EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY
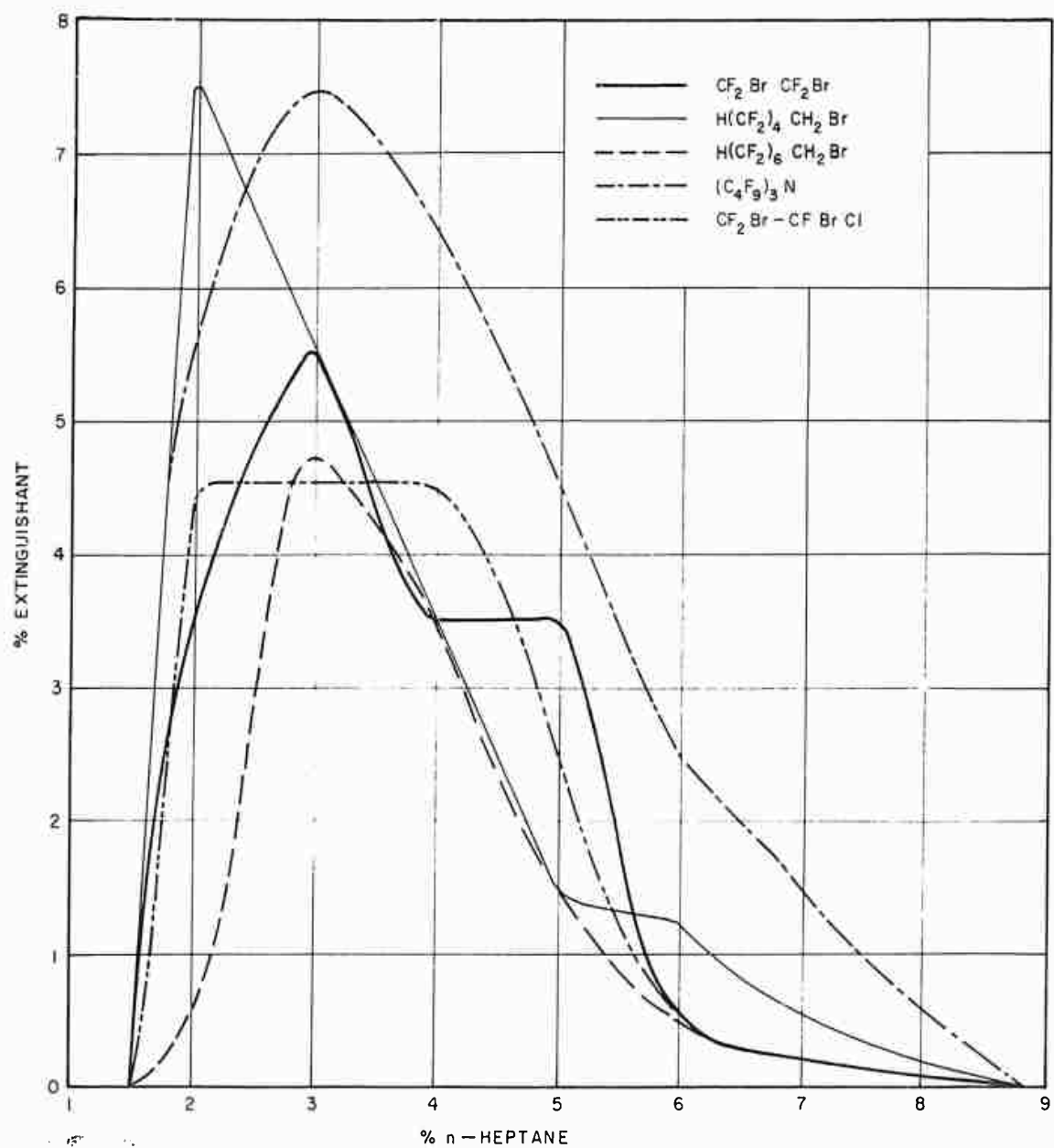OF n - HEPTANE - AIR MIXTURES

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FIGURE 7

EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY
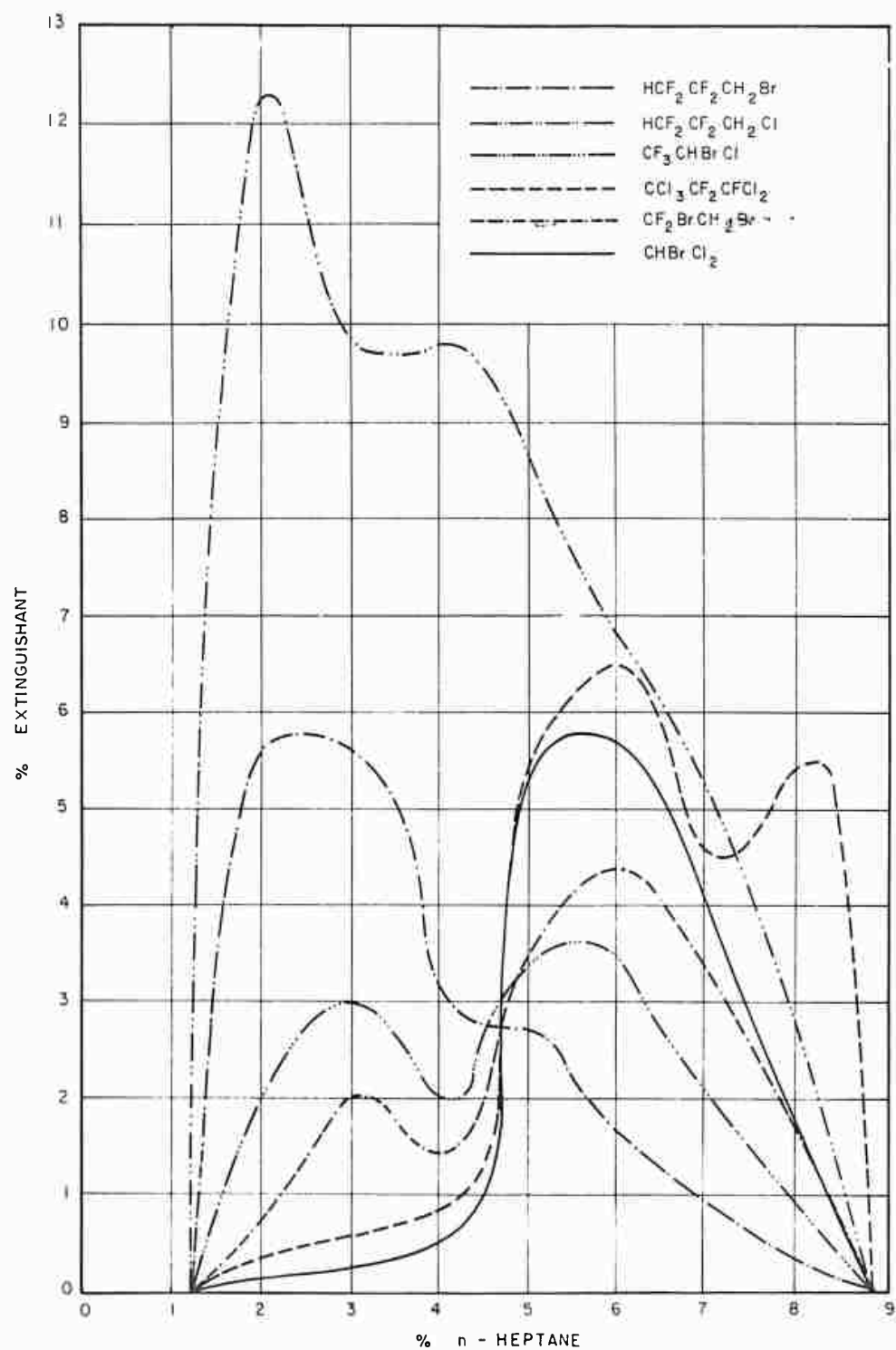OF n - HEPTANE - AIR MIXTURES

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FIGURE 8

EFFECT OF CANDIDATE EXTINGUISHANTS ON
FLAMMABILITY OF n - HEPTANE - AIR MIXTURES

FIGURE 9

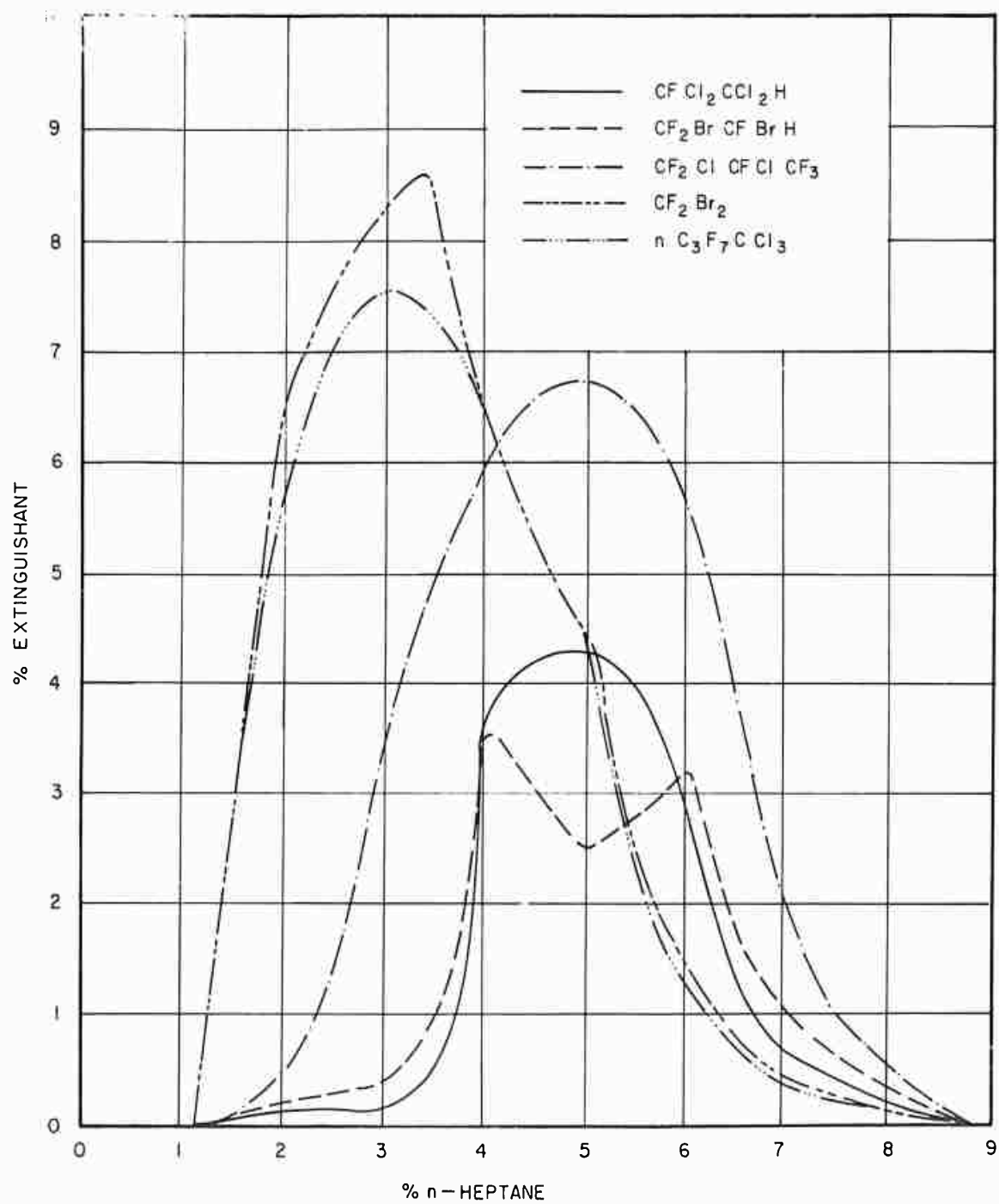EFFECT OF CANDIDATE EXTINGUISHANTS ON FLAMMABILITY.
OF n - HEPTANE - AIR MIXTURES

TABLE IV

EFFECT OF INHIBITORS ON HEPTANE-AIR FLAMMABILITY

Total Pressure 300 mm, Temperature 398°F

	MW	Peak %	Wgt. at Peak %	Rank Wgt. Basis	Rank Vol. Basis
$CF_3CHBrCl$	197.5	3.5	30.7	1	2
$CFCl_2CHCl_2$	186	4.4	36.6	2	4
$CF_2BrCHBrF$	242	3.4	36.8	3	1
$CHBrCl_2$	164	5.5	40.3	4	9
$CBrF_3$	149	6.5	43.2	5	13
$CH_2BrCBrF_2$	224	4.5	45.0	6	5
$CHF_2CF_2CH_2Br$	195	5.2	45.3	7	8
$CBrF_2CClFCF_2CHClF$	314	3.7	51.8	8	3
$CBrF_2CBrClF$	276.5	4.5	55.5	9	6
$CBrF_2CBrF_2$	260	5.5	65.8	10	10
$CClF_2CClFCF_3$	221	6.8	67	11	14
$CCl_3CF_2CCl_2F$	270.5	6.8	78.5	12	15
$CHF_2CF_2CH_2Cl$	150.5	12.3	82.6	13	20
$CHF_2(CF_2)_5CH_2Br$	395	4.75	83.6	14	7
$CF_3CF_2CF_2CCl_3$	287.5	7.5	96.5	15	16
$(CF_3CH_2O)_3PO$	344	6.3	96.7	16	11
$CHF_2(CF_2)CH_2Br$	295	7.5	99.0	17	17
$CHF_2(CF_2)_3CH_2Cl$	250.5	9.3	104.2	18	19
KEL-F-il chloro-fluoroolefin polymer	500 av.	6.5	145.0	19	12
$(CF_3(CF_2)_3)_3N$	671	7.5	219.0	20	18

6. Materials Compatibility

In Table V are shown effects of agents on copper, stainless steel, rubber, neoprene, silicone rubber and teflon. Percentage changes in weight or length are given as well as visual descriptions of the material and agent after thirty days contact at ambient temperatures. Stainless steel and teflon are the only materials completely inert to all of the agents at ambient temperatures. In Table VI are shown effects of moist agents on those materials which were not affected by the dry agents at ambient.

From this screening and a consideration of decomposition temperatures of gasketing materials, it would appear that only Teflon, Viton, Halon, Fluorel, Kel-F and Kynar fluoroplastics and elastomers and perhaps Mylar plastic, are worthwhile testing with dry and moist agents under conditions approaching flight temperatures. Silicone rubber, though having good high temperature properties, is not suitable because it is attacked by these agents.

Metallic materials besides stainless steels for further testing at the more significant flight conditions should include mild steels. Copper may also be tested but appears suspect from its action with the compound $CF_2BrCBrClF$.

7. Cost of Materials

Several potential manufacturers submitted preliminary cost estimates on compounds 2, 4, 5, 7, 8 and 10 of Table I in 5-10 ton quantities. These estimates were given with the understanding that they are only approximate and are not bid prices. Compounds 1, 3, 6 and 9 were prepared by NESCO during this work, are not commercially available and no manufacturer contacted submitted a cost estimate for them. The NESCO estimate is based on a possible price reduction for quantity use of the intermediate alcohols $HCF_2CF_2CH_2OH$ and $H(CF_2)_4CH_2OH$ now available at a development cost of $10.00 per pound from E. I. DuPont. It is also possible that a manufacturer could produce compounds 1, 3, 6 and 9 at lower costs by synthesizing them directly from tetrafluoroethylene and methyl chloride or methyl bromide. These processes and NESCO's processes, to our knowledge, have not been investigated for cost purposes. Compounds 2, 4, 5, 7, 8 and 10 are available from Halocarbon Products, Hackensack, New Jersey. Compounds 5 and 8 are available from Peninsular Chem Research, Gainesville, Florida. Compounds 2 and 5 are available from Columbia Organic Chemicals, Columbia, South Carolina. Compound 8 is available from Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

TABLE V

MATERIALS COMPATIBILITY - DRY AGENTS

Compound	Copper	Stainless Steel	Rubber	Neoprene	Silicone Rubber	Teflon
(1) $H(CF_2)_2CH_2Cl$	n.c. * n.c. **	n.c. n.c.	+6 %, n.c. light amber	-4 %, n.c. light amber	cloudy n.c.	n.c. n.c.
(2) CCl_2FCCl_2H	-0.55 %, green cloudy	n.c. solid residue	gel, not elastic amber	+29.8 %, n.c. amber	dissolved viscous	n.c. n.c.
(3) $H(CF_2)_2CH_2Br$	n.c. n.c.	n.c. n.c.	+16 %, n.c. amber	+4 %, n.c. amber	+33 %, n.c. n.c.	n.c. n.c.
(6) $H(CB_2)_4CH_2Cl$	n.c. n.c.	n.c. n.c.	n.c. light amber	n.c. light amber	+11 %, n.c. n.c.	n.c. n.c.
(7) $CCl_3CF_2CCl_2F$	n.c. n.c.	n.c. n.c.	+102 %, crumbled n.c.	+33 %, n.c. amber	+50 %, crumbled viscous	n.c. n.c.
(8) $CBrF_2CBrClF$	blue coating, n.c. light blue	n.c. n.c.	+66 %, broke easily light amber	+35 %, broke easily light amber	dissolved viscous gel	n.c. n.c.
(9) $H(CF_2)_4CH_2Br$	blk coating, n.c. n.c.	n.c. n.c.	+40 %, n.c. light amber	n.c. amber	+67 %, n.c. n.c.	n.c. n.c.
(10) $CBrF_2CClF-CF_2CClFH$	-0.01 %, n.c. n.c.	n.c. n.c.	+50 %, crumbled amber	+34.5 %, n.c. amber	+46 %, crumbled n.c.	n.c. n.c.

NOTE: Agents were dry and in contact with specimen for 30 days at ambient temperatures.
* This figure is per cent change in specimen and notes condition of specimen.
** This notes condition of agent after contact with specimen.

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TABLE VI

MATERIALS COMPATIBILITY - WET AGENTS

Compound	Copper	Stainless Steel	Rubber	Neoprene	Silicone Rubber	Teflon
$H(CF_2)_2CH_2Cl$	-0.18%, n.c.	n.c.*	n.c.	+4.2%, n.c.		n.c.
	n.c.	n.c.**	light yellow	light yellow		n.c.
$H(CF_2)_2CH_2Br$	n.c., light white coating	n.c.	+1.7%, n.c.	+7.7%, n.c.		n.c.
	n.c.		light yellow	light yellow		n.c.
$H(CF_2)_4CH_2Cl$	n.c., light white coating	n.c.	+4%, n.c.	+4.0%, n.c.	+15%, cloudy	n.c.
	n.c.		light yellow	light yellow	n.c.	n.c.
$CF_2BrCFBrCl$	-0.51%, light blue coating	n.c.				n.c.
	n.c., water blue	n.c.				n.c.

Note: Agents contained liquid water and were in contact with materials for two weeks.

*   This figure is per cent change in specimen and notes condition of specimen.

**   This notes condition of agent after contact with specimen.

8. Toxicity

There do not appear to be any available toxicological data on any of the ten compounds listed in Table I and it is not possible to correlate their structure and toxicity with other halocarbons of known toxic properties. For instance, Engibous and Torkelson (6) quote the Underwriter's Laboratories Classification of Comparative Life Hazard of Gases and Vapors giving a ranking for the series of halogenated methanes as: CCl_4 more toxic than $HCCl_3$, which is more toxic than CH_3Cl, which is more toxic than CH_2Cl_2, i.e., chlorine content cannot be correlated with toxicity.

Only notes of warning can be given as to potential hazard on a structural basis and these warnings should be the subject of experimental toxicological investigation. Compound 2 of Table I is structurally comparable to methylene chloride which is in Underwriter's Group 4. Compound 7 is structurally similar to carbon tetrachloride or chloroform which are in Group 3. Compounds 4, 5 and 8 are structurally similar to dibromotetrafluoroethane which is in Group 4 or 5. Dibromotetrafluoroethane is a liver poison according to Engibous and Torkelson. Compounds 1, 3, 6 and 9 are similar to methyl or ethyl chlorides or bromides, which are in Groups 2 or 4. All the compounds of Table I, however, are of less volatility than the materials cited in Ref. 6 and the possibility of encountering high vapor concentrations with these materials is much less than with the presently used extinguishants.

The higher thermal stabilities of the compounds in Table I compared to known extinguishants which give toxic pyrolysis products should diminish concern over hazards in their use on fires. This is assuming that the acute vapor toxicity of the unpyrolyzed agent is low. Pyrolysis products would be noxious (hydrogen chloride and hydrogen bromide) and would give warning of their presence.

Skin irritation and the toxic effects of skin absorption will be necessary to investigate since the materials in Table I are less volatile than presently used agents. It is well known that materials such as carbon tetrachloride act as liver poisons by skin absorption as well as by inhalation.
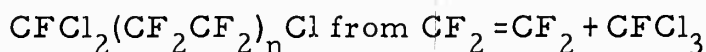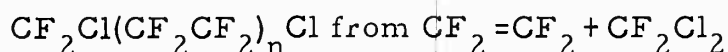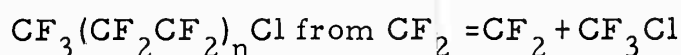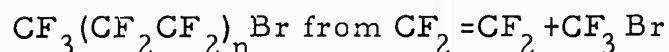
Samples of seven of the compounds in Table I have been submitted for evaluation.

9. Literature Survey

In Table VII are listed compounds abstracted from the complete literature survey which was part of the first quarterly progress report on this contract. On the basis of information obtained during the course of this investigation, these compounds have structures which

should ensure thermal stability in the range $350°F$ to $500°F$. The compounds are known but were not available for testing during this work. If a further choice of potential agents is desired, these compounds may be considered.

In addition, the generalizations on structure and thermal stability in III-C-1 lead to addition of the following compounds with n = 1, 2 or 3, which have not yet been made or reported in the literature, to the list of Table VII.

$$CF_3(CF_2CF_2)_nBr \text{ from } CF_2=CF_2+CF_3Br$$

$$CF_3(CF_2CF_2)_nCl \text{ from } CF_2=CF_2+CF_3Cl$$

$$CF_2Cl(CF_2CF_2)_nCl \text{ from } CF_2=CF_2+CF_2Cl_2$$

$$CFCl_2(CF_2CF_2)_nCl \text{ from } CF_2=CF_2+CFCl_3$$

Unfortunately, no correlation has been found in this work between structure and low temperature properties. Thus the compounds of Table VII and those listed above may prove to be unsatisfactory because of poor low temperature viscosities or because they may be solids above $-70°F$.

It is not recommended that further synthetic or new potential agent screening research be carried out. This reported work indicates that any compound which passed screening has properties which are not ideal in every respect. Each compound is a compromise of the specifications listed in Section II and though it may excel in one detail, it will be less than ideal in another. The same lack of ideality is expected in any of the compounds listed above or in Table VII.

TABLE VII

LITERATURE SURVEY ABSTRACT

UNINVESTIGATED MATERIALS POSSIBLY OF USE

Based on Information Obtained in This Work

Compound	Preparation	BP.°F	FP.°F	Density/°C	Reference
$CCl_2FCClBrCF_3$		268-271			29
$CCl_3CFClCF_2Br$	$CCl_3Br+CF_2=CFCl$	136-145/6mm		1.4673/20	21
$CCl_3CF_2CF_2Cl$		237	-134		30
$CBrClFCFClCFClCBrClF$	$CClFICClF_2+Hg$	273			17
$CBrClFCF_2CF_2CBrClF$	$CBrF_2CClFI+Hg$	167			17
$CBrF_2CFClCFClCBrF_2$	$CF_2BrCHClF+Hg$	167/20mm			14
$CBrF_2CF_2CBrFCF_3$	$CF_3CF=CF_2+CBr_2F_2$	104-122/100mm			19
$CClF_2CClFCClFCClF_2$	$CClF=CClF+F_2$ or $CHCl=CClCCl=CHCl+ClF_3$ or $CF_2=CClF+heat+Cl_2$	273		1.781/20	23, 24, 26, 27, 28
$CCl_3CF_2CCl_2CF_3$	$CF_3CH_2CF_2CH_3+Cl_2$	338	-110	1.813/20	20
$C_4Cl_5F_5$(struct. unk.)		194-198/76mm		1.796/20	26, 27, 28
$C_5BrCl_5F_6$(struct. unk.)		219-239/6mm			21
$CClF_2CF_2CF(CClF_2)_2$		257-259/10			22
$C_5Cl_4F_8$(struct. unk.)		307-8		1.833/20	25
$C_5F_7CBrF_2$		212			14
$CF_3(CF_2)_4CF_2Br$		212-214			15
$CClF_2CClFCCl(CF_3)CClFCF_3$		348-9		1.902/20	25
$CF_3\overset{Cl}{\underset{CCl_2F}{C}} - \overset{Cl}{\underset{CCl_2F}{C}} - CF_3$	$CF_3CCl=CF_2+F_2$	239/20mm		1.942/20	22, 25, 26
$C_6BrF_{10}CF_3$ (1,2)		239			16, 18

D. Synthesis Program

The following compounds were prepared by NESCO during the course of this work. Synthetic methods are outlined for each below and physical properties are given in either Table I or Table III.

1. $H(CF_2)_2CH_2Cl$ was prepared by reaction of $H(CF_2)_2CH_2OH$ with p-toluene sulfonyl chloride to yield the p-toluene-sulfonate ester. The ester was then heated with lithium chloride in diethylene glycol to yield the compound.

2. $H(CF_2)_2CH_2Br$ was prepared by the same method with substitution of potassium bromide for lithium chloride.

3. $H(CF_2)_4CH_2Cl$ was prepared using method 1 with $H(CF_2)_4CH_2OH$.

4. $H(CF_2)_4CH_2Br$ was prepared using method 2 with $H(CF_2)_4CH_2OH$.

5. $H(CF_2)_6CH_2Br$ was prepared using method 2 with $H(CF_2)_6CH_2OH$.

6. $H(CF_2)_8CH_2Cl$ was prepared using method 1 with $H(CF_2)_8CH_2OH$.

7. $BrCH_2CO_2CH_2CF_3$ was prepared from $BrCH_2COCl$ and CF_3CH_2OH.

8. $BrCH_2CO_2CH_2CF_2CF_2H$ was prepared from $BrCH_2COCl$ and $HCF_2CF_2CH_2OH$.

9. $CH_3CBrHCO_2CH_2CF_3$ was prepared from $CH_3CBrHCOCl$ and CF_3CH_2OH.

10. $CF_3CO_2CH_2CH_2CH_2Br$ was prepared from CF_3COCl and $BrCH_2CH_2CH_2OH$.

11. $(CF_3CH_2O)_3PO$ was prepared from $POCl_3$ and CF_3CH_2OH.

12. $(HCF_2CF_2CH_2O)_3PO$ was prepared from $POCl_3$ and $HCF_2CF_2CH_2OH$.

13. Attempts to chlorinate or brominate $H(CF_2)_4CH_2Br$ in the vapor phase utilizing ultra violet light were unsuccessful.

14. Attempts to prepare $(CF_3)_2CBr_2$ from PBr_5 and either $(CF_3)_2C=O$ or $(CF_3)_2CNOH$ were unsuccessful.

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E.   Recommendations

Reasons for recommending work in areas listed here are discussed in individual sections III-C-1 to 8. The items are summarized here.

1.   The list of ten agents of Table I should be narrowed by weighting the importance of properties to obtain a more significant ranking number than given in Table II.

2.   The possibility of utilizing CF_3Br for superior low temperature performance in conjunction with an agent of Table I for high temperature discharge should be investigated. Properties, such as determined in this study, should be determined for such mixtures.

3.   Thermal stability data of more significant relationship to actual environmental conditions of Supersonic Transport agent use and to storage life should be obtained. Effects of water on thermal stability should be determined.

4.   Additives to increase thermal stability of agents should be investigated.

5.   Additives to decrease viscosities and lower surface tensions of agents should be investigated.

6.   Effects of agents and of moisture in agents on materials of construction under flight temperature conditions and under storage life contemplated should be determined.

7.   Actual extinguishant pressures in or above the critical regions should be experimentally determined or approximated by means of an equation of state and critical constants of similar halocarbons. Pressure-fill ratio relationships should be determined at flight temperatures.

8.   Toxicological evaluation.

9.   Fire testing on simulated aircraft fires with those agents or mixtures chosen for final effectiveness testing.

10.   The effect of the agents on titanium alloys which may be used in engines at engine temperatures should be investigated.

REFERENCES

1. Rosser, W. A., Jr., Wise, H. and Miller, J., Seventh Combustion Symposium, Butterworths, London, 1959, p. 175.

2. Lask, G. and Wagner, H. G., Eighth Combustion Symposium, Williams and Wilkins, Baltimore, 1962, p. 432.

3. McBee, E. T. et al, ASTIA Document 114,903.

4. Welch, Z. D., Rosenberg, H. and McBee, E. T., ASTIA Document 136,130.

5. Malcolm, J. E., National Fire Protection Association Quarterly, October 1954.

6. Engibous, D. L. and Torkelson, T. R., WADC-TR-59-463, p. 9.

7. Patterson, A. M., J. Am. Chem. Soc. 55, 3905 (1933).

8. Murphy, C. B., Anal. Chem. 34, 298R (1962).

9. Vassalls, D. A. and Harden, J. C., ibid 34, 132 (1962).

10. Barrall, E. M. and Rogers, L. B., ibid 34, 1101 (1962).

11. ASTM Test Designation D1660-60T, in ASTM Standards, Part 7, Petroleum Products and Lubricants, American Society for Testing and Materials, Philadelphia, 1961, p. 870.

12. Young, E. G., National Fire Protection Association Quarterly October 1954.

13. Kern Chemical Corporation, Los Angeles, California.

14. Haszeldine, R. N., J. Chem. Soc., 1952, 4259,4423.

15. ibid 1953, 3761.

16. ibid 1956, 61.

17. Haszeldine, R. N., British Patent 774,103 (CA 52, 1198 (1958)).

18. Haszeldine, R. N., British Patent 844,604 (CA 55, 7321 (1961)).

19.	Hauptschein, M., Breid, M. and Fainberg, A., J. Am. Chem. Soc. 80, 851 (1958); U. S. Patent 2,975,220, CA 52, 10953 (1958), ibid 55, 15345 (1961).

20.	Henne, A. L., Hinkamp, J. and Zimmerschied, W., J. Am. Chem. Soc. 67, 1906 (1945).

21.	Henne, A. L. and Kraus, D. W., ibid 73, 1791 (1951).

22.	Miller, W. T., Jr., Preparation, Properties and Technology of Fluorine and Organofluoro Compounds , McGraw-Hill, 1951, p. 664.

23.	Miller, W. T., Jr., National Nuclear Energy Series, CA 46, 9988 (1952).

24.	Miller, W. T., Jr., U. S. Patent 2,668,182, CA 49, 2478 (1955).

25.	Miller, W. T., Jr., U. S. Patent 2,716,141, CA 50, 7851 (1956).

26.	Miller, W. T., Jr., U. S. Patent 2,894,042, CA 54, 17265 (1960).

27.	Murray, J. and Wadsworth, K. D., British Patent 774,737, CA 52, 1197 (1958).

28.	Murray, J., J. Chem. Soc. 1959, 1884.

29.	Proben, M., J. Am. Chem. Soc. 73, 4495 (1951).

30.	Tarrant, P., Fluorine Chemistry ed. J. H. Simons, Academic Press, 1951, Vol. 2, p. 272.

Aeronautical Systems Division, Aero Propulsion Lab-
oratory, Wright-Patterson AFB, Ohio. Report Nr. ASD-
TDR-63-804. INVESTIGATION OF FIRE EXTINGUISHING
AGENTS FOR SUPERSONIC TRANSPORT. FINAL REPT.,
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